Pergamon

0277-5387(95)00029-1

Polyhedron Vol. 14, No. 22, pp. 3239–3253, 1995

0277–5387/95 \$9.50+0.00

SILASESQUIOXANES AS LIGANDS IN INORGANIC AND ORGANOMETALLIC CHEMISTRY

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Abstract—Silasesquioxanes are an interesting class of ligands for both main group and transition-metal elements. A variety of coordination environments can be supported by silasesquioxane ligands, and it is now possible to prepare metallasilsesquioxanes containing practically any stable element from Groups 1015. This article surveys the synthesis, characterization, and reactivity of silasesquioxane ligands. Structure, bonding and structural dynamics of both silasesquioxanes and metallasilasesquioxanes are also discussed.

The chemistry of silasesquioxanes and metallasilasesquioxanes can provide important insights into the chemistry of silica and silica-supported transition-metal catalysts. The uniqueness of silasesquioxanes as models for silica is discussed and several systems which provide molecular-level insights into the surface chemistry of silica and silica-supported catalysts are discussed.

Heterogeneous catalysts play a crucial role in the petrochemical industry and catalysts have been developed to catalyse an impressive range of chemical processes ranging from hydrocarbon reforming[1] and oxidation[2] to olefin polymerization[3] and metathesis.[4] The widespread importance of heterogeneous silica-supported transition-metal catalysts has made it desirable to understand the surface chemistry of these species at the molecular level. While surface science has evolved dramatically over the past two decades, current state-of-the-art techniques are still not amenable to detailed mechanistic studies of silica-supported species, and there is considerable debate as to the nature of the active species involved in catalysis. In contrast, homogeneous systems are more easily studied and the chemistry of homogeneous catalysts is easier to delineate. The development of useful homogeneous models for heterogeneous catalysts therefore offers an opportunity to develop a molecular level understanding of heterogeneous catalysts which could lead to better strategies for control of selectivity, activity and catalyst lifetime.

To this end we have focussed considerable effort on the chemistry of incompletely condensed polyhedral oligosilasesquioxanes (POSS), such as those shown below in **1–5**.[5] These molecules are quite attractive ligands for this purpose since they (1) possess sufficient degree of oligomerization as to be relevant models for highly siliceous materials and (2) they retain reactive Si—OH functionality which allows for their exploitation as ligands in a wide variety of main group and transition-metal complexes.

Since POSS such as **1–5** possess an extensive Si—O framework, their electronic properties should be more similar to silica and siliceous solids than conventional models such as simple siloxide ligands [i.e. $(C_6H_5)_3SiO$—]. Using the well-established correlation between ^{13}C chemical shifts and Hammett substituent parameters, we estimate the electron-withdrawing tendency of an Si_8O_{12} framework in **6** below to be remarkably similar to a —CF_3 group.[6] This is in marked contrast to other silyl derivatives (R_3Si), which are electron-donating in nature.[7]

Another failing of conventional models is their inability to mimic the coordination geometry of purported silica-supported species. Most often a metal dictates the arrangement of ligands within its coordination sphere. Subtle changes in this arrange-

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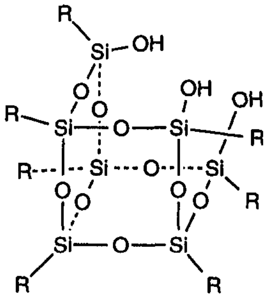
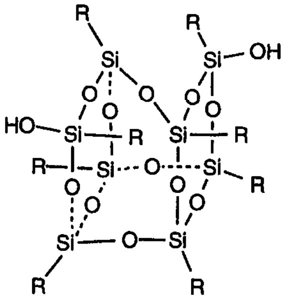
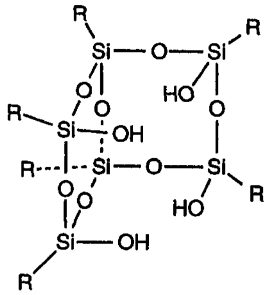


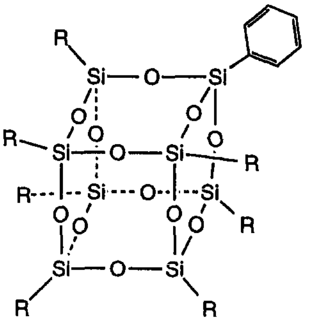
1: R = c-C_5H_9
2: R = c-C_6H_{11}
3: R = c-C_7H_{13}



4: R = c-C_6H_{11}



5: R = c-C_7H_{13}



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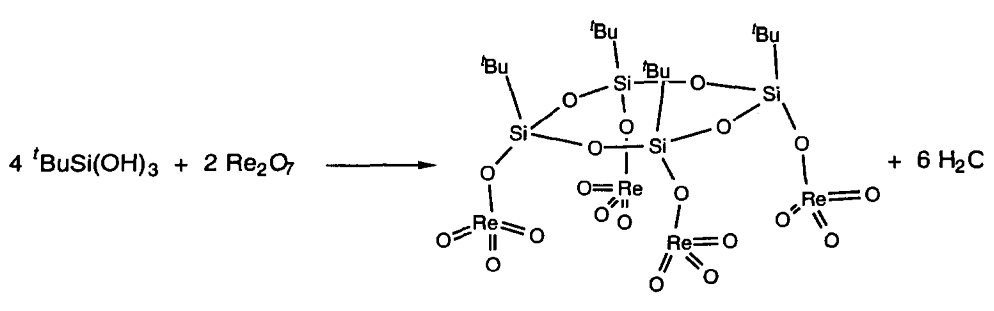
ment, however, can have a profound influence on chemical reactivity, so it is important to develop models which mimic the ability of silica to dictate coordination geometry. The complex (silox)$_3$Ta[8] (silox = ^{t}Bu$_3$SiO—), with its extremely bulky ligands (but which was not actually intended as a model for silica-supported Ta), is trigonal planar: a highly unlikely geometry for any silica-supported metal complex. Similar structural results may be observed with other simple siloxide derivatives. The monodentate nature of these ligands allows far greater mobility within the coordination sphere of the metal which tries to dictate the overall geometry. This is in marked contrast to a silica surface, which is capable of dictating structure because of the relatively inflexible nature of its solid network.

More recent attempts to prepare metallasilasesquioxane model complexes involve the hydrolytic co-condensation of alkyl and aryl silanetriols with metal complexes (eqs 1a and 1b).[9] This approach has the advantage of producing a ligand environment that electronically mimics siliceous materials, but the metal often has a profound influence in directing the condensation process. Very often it is not possible to change the nature of the metal without radically changing the nature of the product. In addition, there is no guarantee that the product(s), whose yields depend almost entirely on their crystallinity (and not their potential importance or relevance), resemble anything close to a silica-supported species.

Incompletely condensed POSS, on the other hand, dictate the coordination geometry of metal complexes much more effectively and show great similarity to purported silica surface sites. As shown

$$NiCl_2 + Na_3O_3SiPh \xrightarrow[\text{reflux}]{n\text{-BuOH/PhCH}_3} \xrightarrow{H_2O/Me_2C{=}O} (PhSiO_2)_{12}Ni_8O_2\cdot(n\text{-BuOH})_4(H_2O)_8(Me_2C{=}O)_2 \quad (1a)$$



(1b)

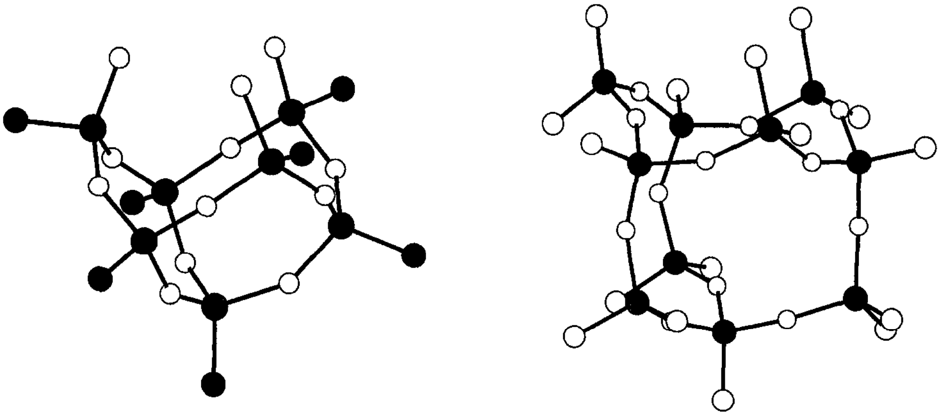


Fig. 1. PLUTO plots (side views) of: (a) trisilanol **2** and (b) the idealized 1,1,1 face of β-cristobalite. Unshaded atoms are oxygen, cross-hatched atoms are silicon, and the shaded atoms are the *ipso* carbons of cyclohexyl groups which are pendant to each silicon in trisilanol **2**. (Data for the structure of β-cristobalite were obtained from Reference 10a.)

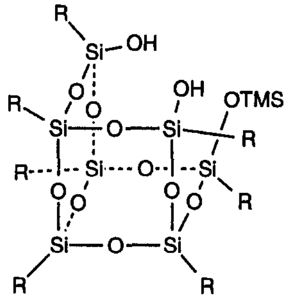
in Fig. 1, trisilanol **2**, whose structure was determined by a single-crystal octahedral face of β-cristobalite[10a] and the idealized (0001) rhombohedral face of β-trydimite.[10b] These crystalline forms of silica (SiO_2) are often implicated as representing the surface structure for amorphous silica.[11] By virtue of their geometric and electronic similarity to silica-supported complexes, transition-metal complexes of POSS should be excellent model systems for heterogeneous silica-supported catalysts.

COMMENTS ON LIGAND SYNTHESIS AND PRODUCT CHARACTERIZATION

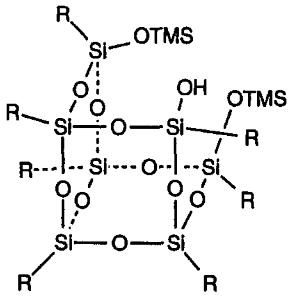
POSS can be obtained from the hydrolytic condensation of $RSiCl_3$ monomers.[5,12] Which polycyclic oligomers are produced depends on many factors: solvent, reaction conditions (temperature, pH) and the nature of the side chain R.[13] With few exceptions the product(s) are intractable mixtures, except for those species which precipitate from the typically polar and strongly acidic medium. As a result, completely condensed species with a *closo* geometry and hydrophobic alkyl groups directed away from the polyhedral core are most often observed.[6,13] However, if the steric parameters for the side chain R and the reaction conditions are just right, incompletely condensed POSS with a high degree of oligomerization are produced (e.g. **1**–**5**). In these cases the products precipitate from solution as strongly hydrogen-bonded dimers. Once again the hydrophobic side chains are directed away from the central core, and the hydrophilic siloxyl groups do not interact with the polar protic reaction medium.

When we initiated our investigations of this interesting class of molecules, there were very few examples of incompletely condensed POSS in the literature. For the higher oligomers which are of particular interest there was only one example wherein Brown and Vogt reported the synthesis of the trisilanol **2** by the controlled hydrolysis of c-$C_6H_{11}SiCl_3$.[12] While this compound is quite useful and is the focal point for much of the chemistry to be described, we were very much interested in developing synthetic routes to other analogues which were more amenable to characterization by NMR spectroscopy and X-ray crystallography. As a result of these efforts, the new trisilanols **1** and **3** were discovered, as well as the tetrasilanol **5**.[14] The diol **4** was discovered as a previously uncharacterized by-product of the hydrolytic condensation of c-$C_6H_{11}SiCl_3$, which also produces **2**.[5]

The trimethylsilyl derivatives **7**–**12** are obtained by amine-assisted trimethylsilylation of the trisilanols **1**–**3** with TMSCl.[15] From a systematic study of the silylation behaviour of silasesquioxanes **2** and **4**, Feher and Newman[15] showed that there is a distinct preference for the silylation of vicinally hydrogen-bonded silanols over isolated non-hydrogen-bonded silanols, especially for reactions carried out in the presence of an amine base such as Et_3N. Most notable was the remarkable selectivity of **2** for monosilylation by one equivalent of TMSCl in 5% Et_3N/THF. Under these conditions **8** is produced in greater than 99% spectroscopic yield (i.e. **11** is produced in less than 1% yield). Subsequent reactions of the monosilyl derivatives **7**–**9** with TMSCl/Et_3N are much less selective and presumably reflect the lower acidity of the siloxyl groups in these derivatives when compared to **1**–**3**, which possess three mutually hydrogen-bonded silanols. In light of Drago's recent study of hydrogen-bonded acid sites on silica,[16] which indicates



7 = (c-C_5H_9)$_7Si_7O_9$(OTMS)(OH)$_2$
8 = (c-C_6H_{11})$_7Si_7O_9$(OTMS)(OH)$_2$
9 = (c-C_7H_{13})$_7Si_7O_9$(OTMS)(OH)$_2$



10 = (c-C_5H_9)$_7Si_7O_9$(OTMS)$_2$(OH)
11 = (c-C_6H_{11})$_7Si_7O_9$(OTMS)$_2$(OH)
12 = (c-C_7H_{13})$_7Si_7O_9$(OTMS)$_2$(OH)

that multiple hydrogen-bonded surface silanols are indeed more acidic than less extensively hydrogen-bonded sites (e.g. "isolated" or vicinally hydrogen-bonded silanols), these results suggest that the silica surface sites that are most reactive towards amine-catalysed silylation are those possessing at least three mutually hydrogen-bonded siloxyl groups.

As is exemplified in **1**–**5**, the optimum conditions for our ligand synthesis involves the use of cycloalkane side chains. While these groups are not ideal for spectral characterization by ^{1}H NMR spectroscopy, the characterization of POSS derivatives is greatly facilitated by the availability of other NMR spectroscopic techniques. Within a given complex there are at least three spin-active nuclei (^{1}H, ^{13}C and ^{29}Si) which can provide structural data, and more may be present depending on the particular derivative. ^{1}H NMR spectroscopy is especially useful for establishing the number of silanols, both hydrogen-bonded (δ 5–7.5 ppm) and isolated (δ 2–4 ppm). It is also useful for determining the number of trimethylsilyl groups (δ 0.0–0.6 ppm, when they are present), which can be easily ascertained since chemical shift ranges for the protons in these groups are far removed from the congested aliphatic region (δ 0.8–2.0 ppm).

Barring unexpected complications, such as coincidental signals, the symmetry of POSS complexes may be readily identified by either ^{13}C NMR or ^{29}Si NMR spectroscopy. The application of ^{29}Si NMR spectroscopy to this problem is clear, but the utility of ^{13}C NMR spectroscopy may not be as obvious. The presence of numerous resonances in a narrow chemical shift range due to the aliphatic cycloalkane groups may at first appear to present a problem. However, the *ipso* carbon atoms (those bound to silicon) generally occur in a different region (δ 22–25 ppm) from the remaining CH_2 groups (δ 26.5–30 ppm). Also, the number and relative ratios of CH groups (again the *ipso* carbon atoms) may be readily determined by the use of the DEPT90 pulse sequence. The use of ^{13}C NMR spectroscopy is particularly convenient, since many high field spectrometers are configured to record spectra of this nucleus on a routine basis. The ^{1}H, ^{13}C and ^{29}Si NMR spectra of **2** (C_{3v} symmetry) are shown in Fig. 2 as an example of the application of this analytical technique to the characterization of POSS.

GENERAL SYNTHETIC CONSIDERATIONS

During the course of our investigations we have developed numerous strategies for the synthesis of POSS complexes and have also discovered a few pitfalls. Three techniques have been utilized extensively for the synthesis of heteroatom and transition-metal containing silasesquioxanes: (1) the direct metathetic reaction between silanols and less acidic alkyl, amide or alkoxide ligands, (2) amine-assisted metathesis of metal–halide complexes and (3) metathetic replacement of M—halide bonds by silasesquioxide anion "equivalents." These are shown in eqs (2)–(4), respectively.

The direct reaction of silanols with basic alkoxide, amide or alkyl ligands allows the synthesis of a great many interesting metallasilasesquioxanes but is limited by the availability of an appropriate metal complex. Protonolysis of metal alkyl complexes works well for the electropositive metals (e.g. Zr, Ti, Al, Ga) but fails for the less reactive M—C bonds of the late transition metals (i.e. $CpPt(CH_3)_3$ and Me_3ReO_2) or the moderately electropositive main group elements (i.e. BEt_3).

The amine-assisted metathesis of SiO—H for L_nM—X bonds is quite convenient and has proven to be the most effective method for the synthesis of POSS complexes. Utilizing this strategy the trisilanol **2** has been "capped" with a

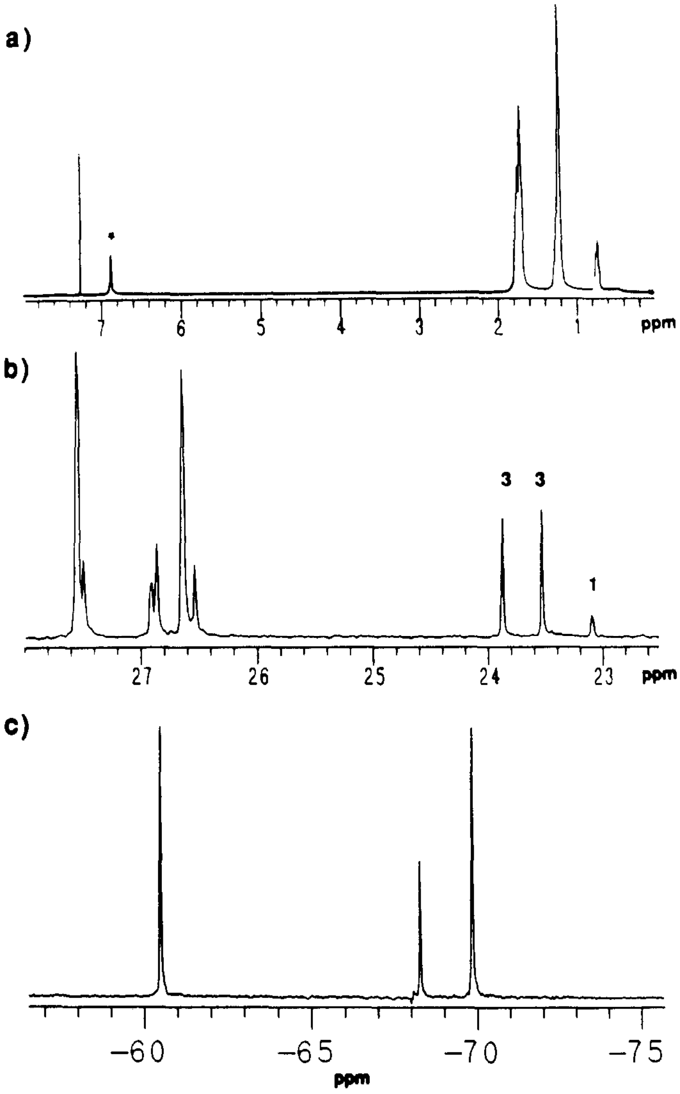
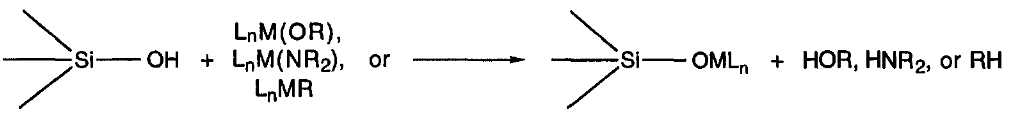
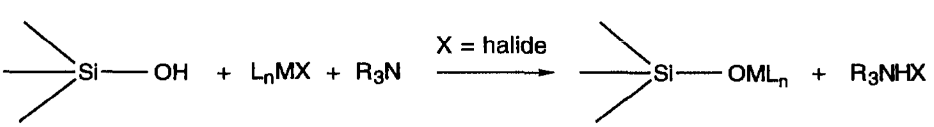


Fig. 2. Nuclear magnetic resonance spectra of trisilanol **2**: (a) ^1H spectrum at 500 MHz; hydrogen-bonded silanols marked with an asterisk, (b) ^{13}C spectrum at 125 MHz; *ipso* carbon atoms marked, (c) ^{29}Si spectrum at 99 MHz. All spectra were recorded in $CDCl_3$ solution at room temperature (~20°C).



(2)



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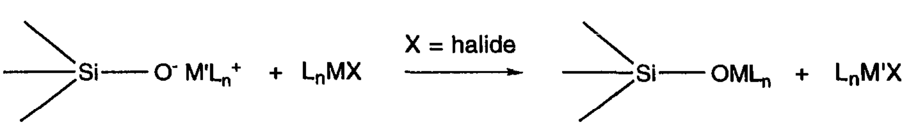
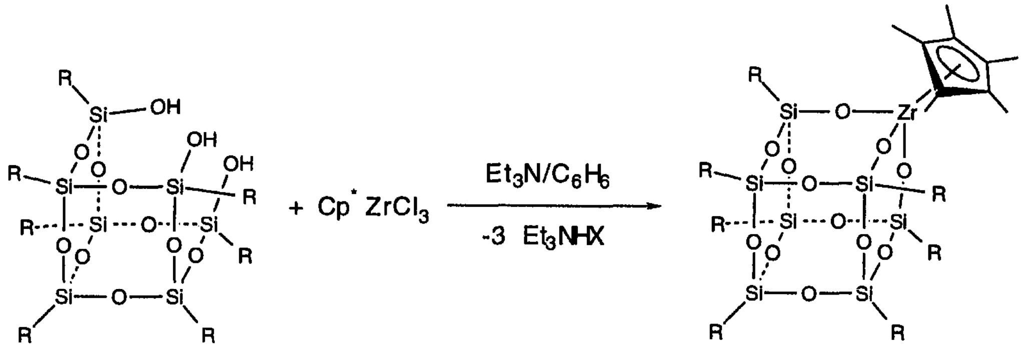


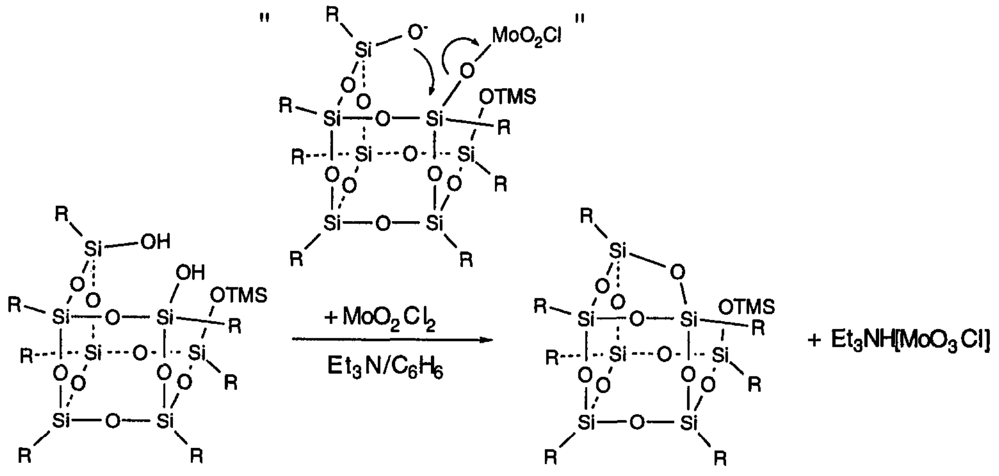
(4)

variety of reagents including, but not limited to: O=VCl_3,[17] Cp^*ZrCl_3,[18] $CpTiCl_3$, $TiCl_3(NMe_3)_2$,[19] $VCl_3(NMe_3)_2$,[20] $CrCl_3(NMe_3)_2$,[20] $RSiCl_3$ (R = H, aryl, alkyl, Cl),[5] $MeGeCl_3$,[5] $RSnCl_3$ (R = Me, Ph),[3] PCl_3,[21] $AsCl_3$,[21] $SbCl_3$,[21] BI_3,[22] $AlCl_3$,[23] $GaCl_3$,[23] and GaI_3.[23] This procedure is exemplified in equation (5).[18]



(5)

A common side reaction, however, is the base-assisted cyclodehydration of the silasesquioxane, as shown in eq. (6). This is most commonly observed for high valent L_nMX and explains the failure of **1** and its analogues to react cleanly with MoO_2Cl_2,[24] CrO_2Cl_2[24] and O=PCl_3.[21] In these cases it is quite clear that the potential capping group is also an excellent leaving group, and this presumably influences the course of the reaction, which proceeds as shown.



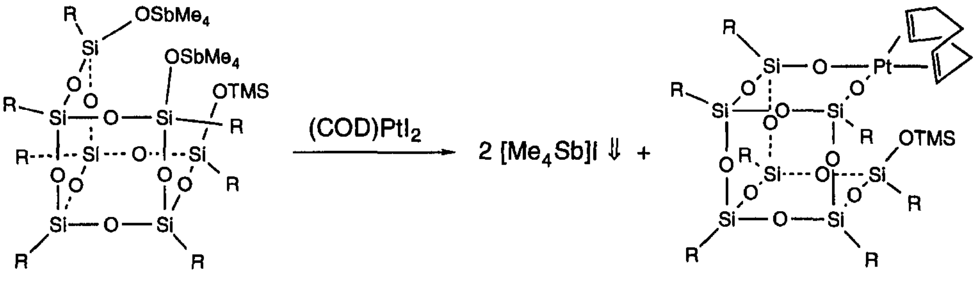
(6)

One way of circumventing this problem involves the oxidation of lower valent heteroatom and transition-metal containing POSS. The potential of this method was demonstrated by the successful preparation of phosphate ester **14** (eq. 7),[21] which is formed in low yield (~20%) from **2** and O=PCl_3 in Et_3N/C_6H_6. In contrast, phosphite **13** is formed in >95% yield from the reaction of **2** and PCl_3 under identical conditions.[21] Oxidation of **13** with ozone affords **14** in nearly quantitative yield.

The problems associated with the above two procedures led us to explore the reaction of anionic equivalents of silasesquioxanes **1–5**. We were particularly interested in this procedure since it is by far the most common method for synthesizing metal complexes of alkoxides and siloxides, especially those derived from the relatively non-reactive late transition-metal halides.[25] A major hurdle was the susceptibility of these frameworks toward cleavage and/or polymerization by moderately nucleophilic reagents.[13,26] Thus, while deprotonation of the trisilanols **1–3** with one equivalent of NaO^{t}Bu affords the mono-sodium derivatives cleanly, the product is only stable for brief periods of time in solution.[27] Furthermore, attempts to exhaustively deprotonate the siloxyl groups resulted in the decomposition and presumed skeletal degradation of the silasesquioxane framework.

Softer anion sources, such as those derived from thallium(I) or tetraalkylstibonium siloxides, however, do not promote skeletal rearrangements and are excellent latent sources of silasesquioxide anions.[28] As such, they have proven quite useful

$$2 + PCl_3 \xrightarrow[-3Et_3NHCl]{Et_3N/C_6H_6} \underset{\textbf{13}}{(c\text{-}C_6H_{11})Si_7O_9(O_3P)} \xrightarrow{O_3/CH_2Cl_2} \underset{\textbf{14}}{(c\text{-}C_6H_{11})Si_7O_9(O_3P{=}O)} \qquad (7)$$



(8)

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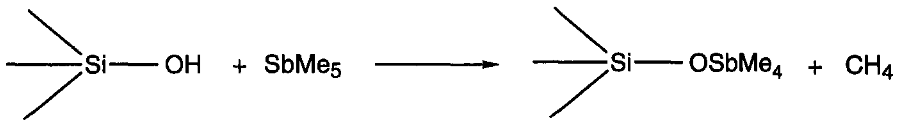
reagents for the synthesis of metallasilasesquioxanes such as the Pt^{II}(COD) derivative **15** below (eq. 8).[28a] These "anionic" silasesquioxanes are readily prepared by the reaction of the parent silanols with Tl(OEt)[28a] and $SbMe_5$, respectively.[28b]

The reactions of incompletely condensed silasesquioxanes with $SbMe_5$ are particularly notable because they are selective for exactly one methyl group in the antimony reagent (eq. 9).[29]



(9)

In addition, trisilanol **2** again appears to be much more reactive than other incompletely condensed silasesquioxanes with fewer than three mutually hydrogen-bonded siloxyl groups.[28b] In particular, while the reaction between one equivalent of $SbMe_5$ and **2** (both 0.01 M) proceeds to completion in 3 min or less at room temperature, subsequent stibnation by $SbMe_5$ requires much more vigorous reaction conditions (excess $SbMe_5$ 2–4 h at 50–60°C). The partially trimethylsilylated analogues **7–12** required similarly vigorous conditions for exhaustive stibnation of their siloxyl groups. This has important implications for the chemistry of silica surfaces and further supports the assertion that more extensive hydrogen-bonded silica surface sites are both more acidic and reactive towards a variety of reagents than less extensively H-bonded surface sites (e.g. isolated monosilanols and both vicinally and geminally H-bonded disilanols).

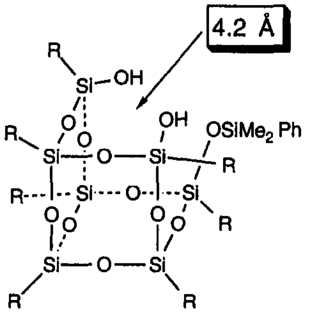
COMMENTS ON STRUCTURE AND BONDING

The ability of POSS such as **1–5** to complex a wide variety of L_nM fragments is now well-precedented. Fragments as diverse as "CpZr" (Zr covalent radius = 1.45 Å)[30] and "P" (P covalent radius = 1.06 Å)[30] are easily accommodated by the silasesquioxane framework in **2** due to the flexible nature of the Si—O—Si backbone. While Si—O bond distances are "inflexible" and span a narrow range (1.60–1.64 Å), the Si—O—Si flexing potential is very broad and shallow. The net result is that Si—O—Si bond angles span a very large range (from 135° to 180°) with a theoretically calculated energetic minimum near 150°.[31] As an example of this flexibility, we note that the siloxide Si atoms closest to the binding cavity in trisilanol derivatives of **2** may be separated by as little as 4.2 Å as is found in **16** (which crystallizes as a hydrogen-bonded dimer)[5] or as much as 5.5 Å as is observed in **17**.[23]

These values may be compared to the observed siloxyl group (Si—Si) distance in **2** of 4.9 Å[5] and β-cristobalite, which is 5.04 Å.[10a]

Monomeric versus dimeric structures

One of the more exciting possibilities for POSS chemistry was the potential of the ligand to dictate unusual coordination geometries. We originally anticipated that trivalent ions, such as V^{III} or Al^{III}, would react with trisilanols such as **2** to form complexes with low coordination number (due to the steric bulk of the aliphatic periphery) and a pyramidalized geometry (due to the unique nature of the binding cavity). Such a species should be exceptionally reactive. Instead, our efforts were thwarted



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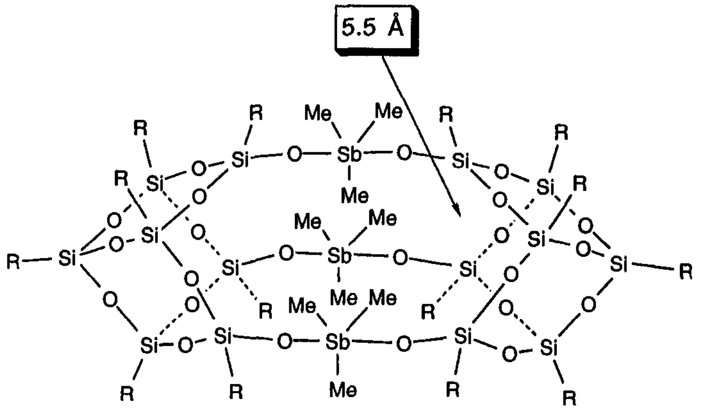

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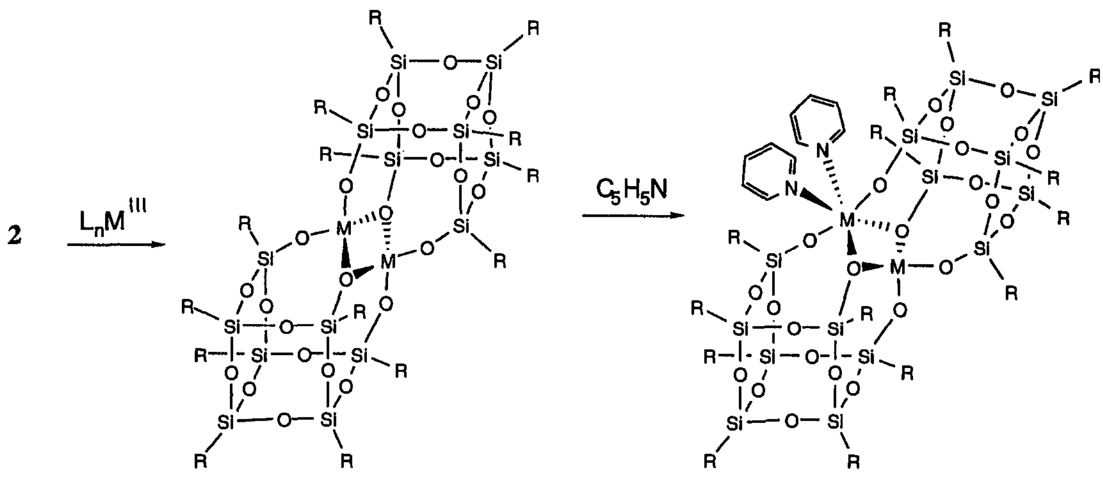
by the flexibility of the cage framework, which allowed these ions to attain higher coordination numbers through dimerization. Structures such as **18**^{19,20,31} and **19**^{19,20} below, as well as **17**^{23} above (all confirmed by single-crystal X-ray diffraction studies), are representative of this ability.

Even a trigonal planar arrangement of siloxide oxygen atoms, which is energetically preferred for trisiloxyboranes, is attainable through dimerization (see **20**).^{22} The steric bulk of (c-$C_6H_{11})_7Si_7O_9(OTMS)_2(OH)$, **11**, however, results in the isolation of a mono-valent thallium derivative with the very unusual coordination number 2 for each Tl^I centre within the dimer (see Fig. 3).^{23,28a} These structural observations have also been confirmed by single-crystal X-ray diffraction.

Structural dynamics

The flexibility of the cage frameworks in heteroatom and transition-metal derivatives of POSS are further demonstrated by the dynamic behaviour shown by many of these complexes. So, for instance, the borane derivative **20**^{22} and the Mo≡Mo-bonded derivative **21**^{34} exhibit fluxional behaviour. At high temperature each complex exhibits apparent C_{3v} symmetry. At low temperature the dynamic exchange of siloxide groups is slowed relative to the NMR time-scale and the spectra are consistent with the C_s symmetric structures which are observed in the solid state.^{22,34} For **20**, simulation of the lineshapes in both the $^{13}C\{^1H\}$ and $^{29}Si\{^1H\}$ NMR spectra allowed determination of



M = Al,^{31} Ga,^{23} Ti,^{19} V,^{20} Cr^{20}

18

M = Ti,^{19} V,^{20} Cr^{20}

19

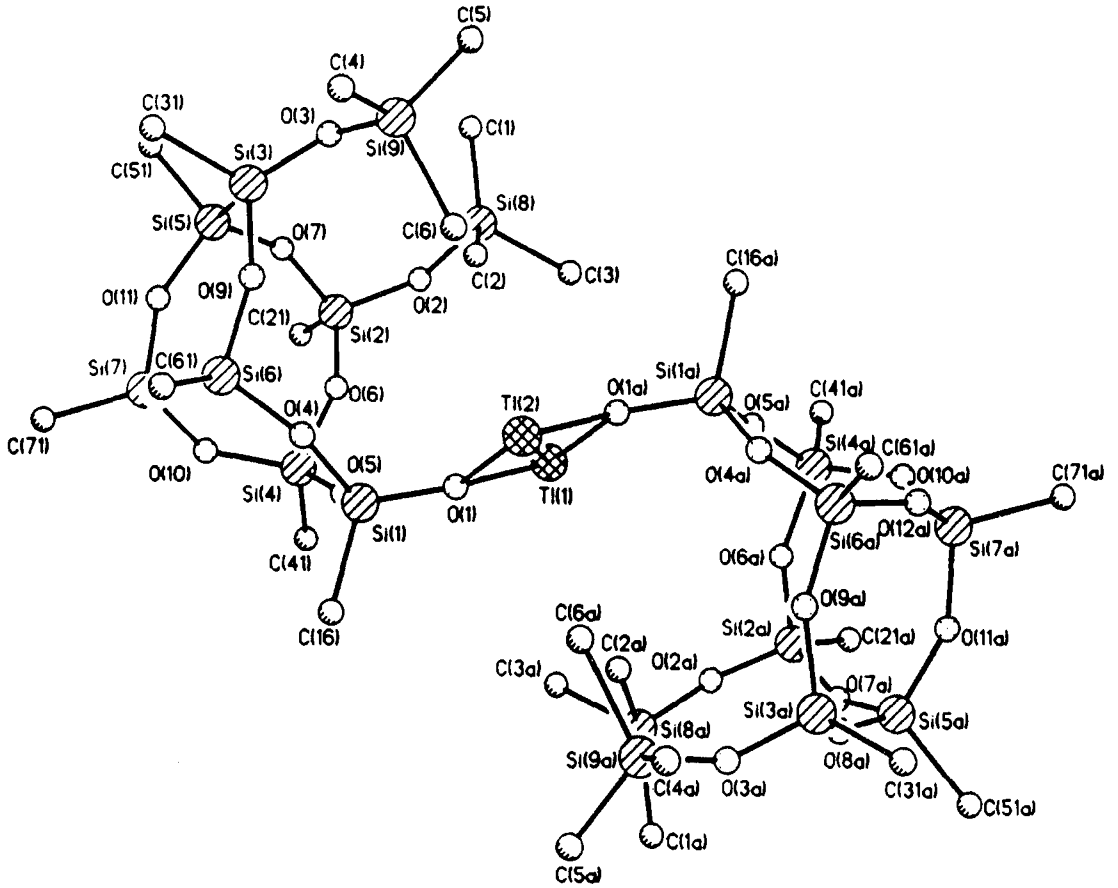
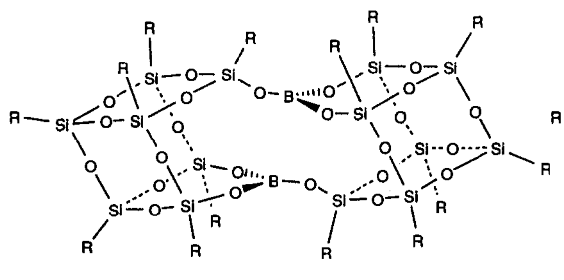


Fig. 3. PLUTO plot of the silasesquioxide $(c\text{-}C_6H_{11})_7Si_7O_9(OTMS)_2(OTl)$ showing its unique dimeric structure. Only the *ipso* carbon atoms of the cyclohexyl rings are shown for clarity.

$\Delta H‡ = 9.1 \pm 0.3$ kcal mol^{-1} and $\Delta S‡ = -17 \pm 2$ eu for the exchange process.[34]

Another example of dynamic behaviour exhibited by metallasilasesquioxanes involves aggregation. The vanadate ester $(c\text{-}C_6H_{11})_7Si_7O_9(O_3V{=}O)$, which may be prepared by any of the general synthetic strategies discussed above from $(Pr^iO)_3V{=}O$, $(TMSCH_2)_3V{=}O$ or $Cl_3V{=}O$, exists as a mixture of monomer, **22**, and dimer, **23**, in solution.[17] From temperature-dependent measurements of the equilibrium constant (eq. 10), the thermodynamic parameters were determined: $\Delta H = -6.0(3)$ kcal (mol^{-1} and $\Delta S = -17(1)$ eu.[17] Attainment of the equilibrium is slow at low temperature or in cases where traces of moisture are rigorously excluded, but is chemically rapid at room temperature or above. The disparity in structure between **22** and **23** (which is not a simple aggregate of two molecules of the former) necessitates significant structural changes to affect their interconversion. This behaviour is reminiscent of the fluxionality exhibited by both **20** and **21** and



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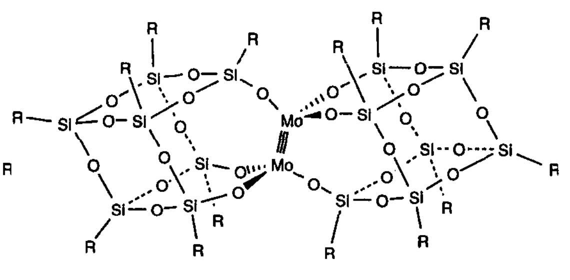

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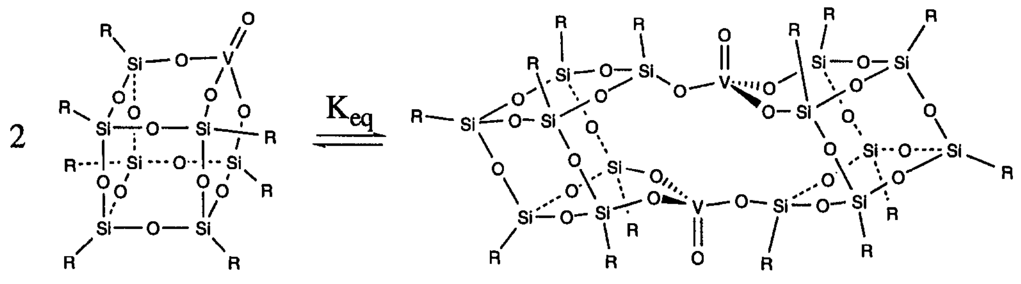


22 **23** (10)

presumably reflects the ease with which skeletal deformation of the silasesquioxane frameworks in these complexes occurs.

Bonding considerations: O-p_π *donation in silasesquioxane complexes*

The M—O bond distances in transition-metal derivatives of POSS may be taken as a good indicator of the strength of the metal–ligand bonds, and may reflect the degree to which filled O-p_π to empty M-d_π interactions occur. As has already been stated, the potential energy surface for Si—O—Si angular deformation is broad and shallow, and this is also true for Si—O—M. While linear Si—O—M linkages result in a degeneracy in the oxygen lone pair orbitals, which makes them both available for π-donation, obtuse Si—O—M angles do not necessarily indicate strong interactions between oxygen and M in these complexes. In fact, there is very often little correlation between M—O—R angle and M—O distance.[35] This is especially true for metallasilasesquioxanes, since the size of the metal often determines the Si—O—M angle from geometric considerations.

Based on the numerous single-crystal X-ray diffraction studies that have been performed on metallasilasesquioxanes, it is apparent that these ligands do not produce electron-rich complexes, especially when compared to other siloxide or alkoxide ligands. For instance, in a series of triphenylphosphine-oxide complexes of aluminium, the observed Al—O(P) distance may be taken as an indication of the electrophilicity of the Al centre, and as a consequence reflects on the nature of the other ligands present about this metal. The data[36,37] (reproduced in Table 1) indicate that the Al centre in the silasesquioxane complex[32] is much more electrophilic than the corresponding trimethylsiloxy derivative $(TMSO)_3Al$.[36] Not surprisingly, there is no correlation between Al—O—P angle and Al—O(P) distance.[36] There is an excellent correlation between Al—O(P) distance and ^{31}P chemical shift,[36] however, and this may reflect the degree of electronic delocalization in the linkage.[38]

From transition-metal chemistry, where π-bonding into empty M-d_π orbitals is important, we have several examples. For instance, the Mo—O distances in the low temperature (−169°) structure of **21**[34] are 0.02 Å longer than those observed in $Mo_2(OCH_2{}^tBu)_6$, whose structure was determined at room temperature.[39] Vanadate ester **23** exhibits a V═O bond length that is 0.01 Å shorter than the triphenylsiloxy derivative $(Ph_3SiO)_3V{=}O$.[17] This contrasts with the (Si)—O—V separations, which are 0.01 Å longer for **23**.[17] Similar structural effects are observed in the solid state for the chromate ester of $(c\text{-}C_6H_{11})_7Si_7O_9(OTMS)(O_2CrO_2)$ (**24**)[40] vs $(Ph_3SiO)_2CrO_2$.[41] While these effects are very small, and not outside the statistical limits of significance, the pattern is in all cases consistent with a diminished capacity for siloxyl-O-p_π to M-d_π donation in POSS derivatives. It is especially significant that competitive π-donors show signs of increased M—L interactions in the presence of POSS co-ligands when compared to simple siloxide and alkoxide analogues. As another example of this effect, one may compare the W—N bond distances in a series of amido complexes of W^{VI} (Table 2).[42] The oxygen atoms in the silasesquioxane derivative **25**[41] (Fig. 4) are clearly inferior π-donors compared to —NMe_2 ligands,[43] but are apparently superior in this regard to a carbamato (η^1-O_2CNMe_2) linkage.[44]

CATALYTIC ACTIVITY OF METALLASILASESQUIOXANES

Olefin polymerization

Silica-supported catalysts (especially those derived from chromium) are used extensively for the coordination polymerization of ethylene.[45] The commercial importance of these systems has led to an intense research effort aimed at elucidating the detailed chemistry of these species at the molecular level. Despite this, the mechanism(s) by which het-

Table 1. Data for Ph_3PO adducts of aluminium : $Ph_3PO—AlX_3$

X	Al—O(P)	P—O	P—O—Al	$\delta\ {}^{31}P$	Ref.
$O_3Si_7O_9$	1.770(5)	1.508(4)	160.4(3)	42.2	30
Cl	1.733(4)	1.519(4)	180	44.9	35
Br	1.736(4)	1.513(7)	180	45.7	35
OTMS	1.807(4)	1.517(4)	146.7(2)	40.6	34
Me	1.837(2)	1.500(2)	180	36.5	34

Table 2. W—N distances in W^{VI} amido complexes

Complex	W—NMe_2 distance (Å)	Ref.
$W(NMe_2)_6$	2.032(3)	41
$W(\eta^1\text{-}O_2CNMe_2)_3(NMe_2)_3$	1.922(7)	42
$(c\text{-}C_6H_{11})_7Si_7O_9(O_3W(NMe_2)_3)$, **25**	1.958(5)	40

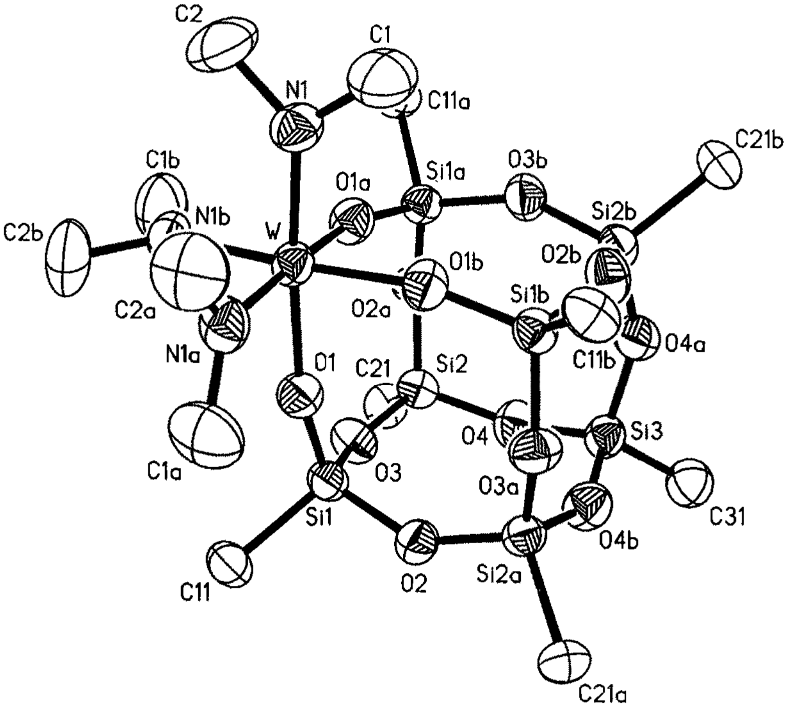


Fig. 4. ORTEP drawing of the tris-amido complex **25**. Ellipsoids are shown at the 40% probability level and only the *ipso* carbon atoms are shown for clarity.

erogeneous catalysts form, function and decay are often unclear and highly controversial.[45b] The problems associated with the study of these heterogeneous systems are exacerbated by the lack of structurally relevant, well-defined homogeneous model systems.

With this in mind, we were particularly interested in investigating the activity of the vanadate esters **22** and **23** and the chromate ester **24** as olefin polymerization catalysts in the presence of aluminium alkyl co-catalysts. The findings were remarkable testimony to the unique nature of metallasilasesquioxanes.[40,46]

Both **22** and **24** are active pre-catalysts for the formation of linear high-density PE when 2–10 equivalents of $AlMe_3$ are added under an ethylene atmosphere.[40,46] (The dimer **23** is not directly involved in the catalytic sequence but is a precursor to **22**.) The physical characteristics of the PE produced are shown in Table 3. Under bench top reaction conditions, ethylene uptake virtually ceases upon gelation of the polymerization medium, suggesting that this is the factor which limits $\bar{M}_w$ to ~45,000. Under high pressure reaction conditions, $\bar{M}_w$ increases by a factor of 10.

In contrast to the activity exhibited by **22**/$AlMe_3$ or **24**/$AlMe_3$, simple siloxide analogues such as $(Ph_3SiO)_3V{=}O$ or $(Ph_3SiO)_2CrO_2$ show little or no activity towards olefin polymerization under identical conditions.[40,46]

Based on careful spectroscopic analysis of low temperature mixtures of $Al(CH_2TMS)_3$ and vanadate **22**, a reaction sequence (eq. 11) involving successive alkyl transfers and coordination of the $L_nV{=}O$ bond to the Lewis acidic Al centres was implicated as leading to the active catalyst.[47] The reaction sequence also accounts for the observed dependence of catalyst activity (as measured by turnover number) on $[AlR_3]$ reagent, which is maximized when ~2 equivalents of aluminium alkyl co-catalyst are added.[40,46] Larger amounts of AlR_3 result in reduction and deactivation of the metal centres, while fewer equivalents are not sufficient to affect complete catalyst activation. (One equivalent of $Al(CH_2TMS)_3$ is apparently consumed by oxygen and moisture under the extremely dilute reaction conditions.)

Similar activity enhancement is observed when mixed alkyl/siloxide complexes $(Ph_3SiO)_n(TMSCH_2)_{3-n}V{=}O$ are employed.[48] While these are not nearly as effective catalyst precursors, catalyst efficiency (as measured by catalyst lifetime and turnover number) is maximized when $(TMSCH_2)_3V{=}O$ is reacted with $(TMSCH_2)_3Al$ under an atmosphere of ethylene.

Olefin metathesis

Olefin metathesis is catalysed by a great many alkylidene complexes, most notably for those of tungsten and molybdenum.[4,49] Many factors influence the activity of these species, but in the well known class of catalysts developed by Schrock, it is quite apparent that the presence and type of π-donor alkoxide ligands is very important, with the best catalysts being derived from the strongly σ-withdrawing hexafluoro-t-butoxide ligand (i.e. $[(CF_3)_2(CH_3)CO]_2M({=}CHR)({=}NAr)$; M = Mo, W).[50]

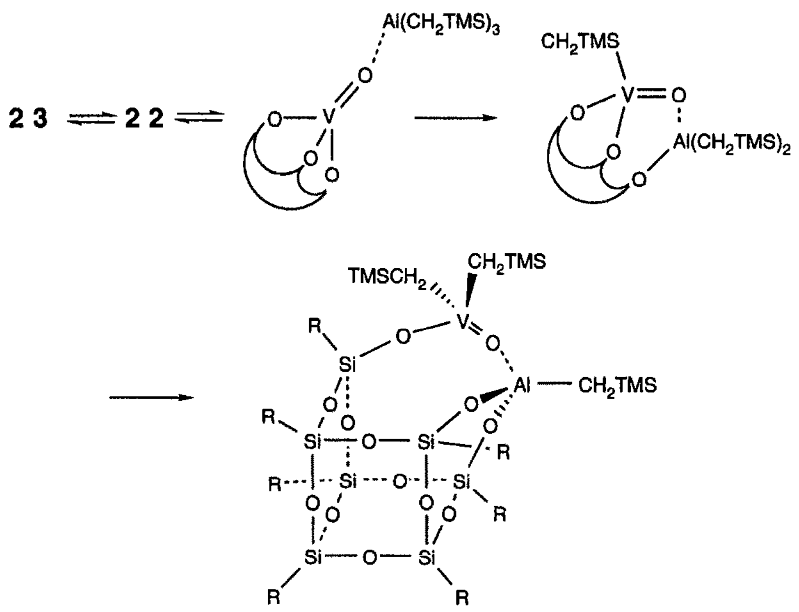
With these observations in mind, the unique combination of steric and electronic properties exhibited by POSS led us to explore this class of ligands as spectator groups in olefin metathesis catalysts. The preparation of a suitable Mo or W alkylidene complex originally presented a significant synthetic challenge, since the high oxidation state of the Mo and W precursors promoted the previously described cyclodehydration of silasesquioxanes. We overcame this obstacle by employing the bis-Tl derivative $(c\text{-}C_6H_{11})_7Si_7O_9(OTMS)(OTl)_2$, **26**, in conjunction with $Mo(CHCMe_2Ph)(NAr)(OSO_2CF_3)_2(dme)$, as shown in eq. (12).[51] The product **27** may exist as any one of four isomers (alkylidene *exo* **27a** or *endo* **27b**, plus the other 180° alkylidene rotamer for each) but only one is observed by ^1H NMR spectroscopy. While rapid $Mo{=}C$ bond rotation may account for our failure to observe rotamers, this process must be fast relative to the NMR time-scale, even at −50°C, and as such would be unprecedented.[50]

The lack of structural data notwithstanding, we can state conclusively that **27** is an excellent catalyst for the metathesis of olefins.[51] When 4800 equivalents of 1-octene are added to a catalytic amount of **27** in C_6D_6, 150 turnovers occurred within 20 s of mixing. Furthermore, while ethylene accumulation slows the productive metathesis of 1-octene to 7-tetradecene, purging the system allowed their complete interconversion. Similar results are obtained for 1- and 2-pentenes as well as *cis*-2-octene. In sealed tube reactions where ethylene is not purged, the system remains active for long periods (1.5 days, 25°C).

The ability of **27** to tolerate a wide variety of functional groups suggested that it might be able to metathesize functionalized olefins. We find that 400

Table 3. Physical properties of polyethylene from POSS-derived catalysts

Catalyst	Co-catalyst	$\bar{M}_w$	$\bar{M}_n$	T_m	P.D.I.	$P_{(olefin)}$ (atm)
24	$AlMe_3$	376,000	61,400	132.1	6.13	38
24	$AlMe_3$	30,680	8,890	130.7	3.45	1
22	$AlMe_3$	47,900	21,000	131.6	2.28	1
22	$Al(CH_2TMS)_3$	128,500	22,470	133.9	5.72	1



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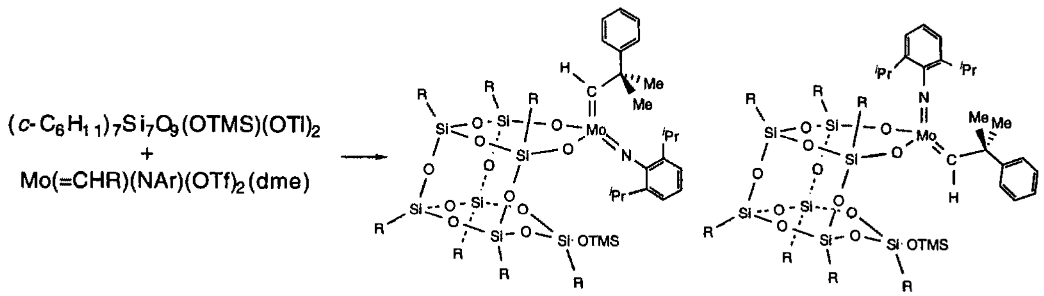

27a **27b**

(12)

equivalents of methyl oleate are metathesized within 2 h at room temperature, and the system remains catalytically active for at least 24 h.[51]

These results, though of a preliminary nature, present a number of new and exciting possibilities for the development of metathesis catalysts which are currently under exploration.

CONCLUDING REMARKS

The nature of the ligands present within the coordination sphere of a metal has a profound influence on its reactivity. In the field of alkoxide chemistry this is especially apparent, since the RO— family of ligands may be varied systematically by changing R. The pioneering work of Chisholm is noteworthy in this regard.[52] Whereas $W_2(O^tBu)_6$ reacts with a single equivalent of carbon monoxide to produce an adduct which shows substantial reduction of the C≡O bond ($\nu(CO) = 1575\ cm^{-1}$), the corresponding fluoroalkoxide complex $W_2(OC(CF_3)(CH_3)_2)_6$ or the siloxide complex $W_2(OSi^tBuMe_2)_6$ provide no evidence for mono-carbonyl adduct formation.[53] Instead, reversible binding of 2 equivalents of CO yield 1,2 adducts that exhibit very little reduction of the C≡O bonds as determined by IR spectroscopy.[53] Similar dramatic effects are observed in the reactivity of these complexes with small unsaturated molecules such as allene, olefins and alkynes.[52,54]

Other examples readily come to mind, including the aforementioned work of Schrock concerning olefin metathesis.[50]

As a dramatic example recently described by Bergman, the complex *cis*-$(PPh_3)_2Re(CO)_3(OMe)$ reacts with CO_2 at $-40°C$ to give *cis*-$(PPh_3)_2Re(CO)_3(O_2COMe)$ by direct insertion of the electrophile into the Re—OMe bond.[55] In contrast, the phenoxide derivative *cis*-$(PPh_3)_2Re(CO)_3(OPh)$ forms the analogous CO_2 insertion product much more slowly (7 days, 100°C) by a pathway that apparently involves prior dissociation of a phosphine ligand.[55]

These examples highlight the dramatic effects that slight changes in the nature of R may have on the overall reactivity of an alkoxide (siloxide) complex. The catalytic activity exhibited by metallasilasesquioxanes (olefin polymerization and metathesis) is a harbinger of new manifolds of reactivity that may be observed by the continued exploration of this family of complexes. We look forward to describing the results of this systematic exploration in the future.

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